ENVIRONMENTAL ANALYSIS

ANALYSIS OF OIL IN WATER USING THE AGILENT CARY 630 FTIR

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Solution Note

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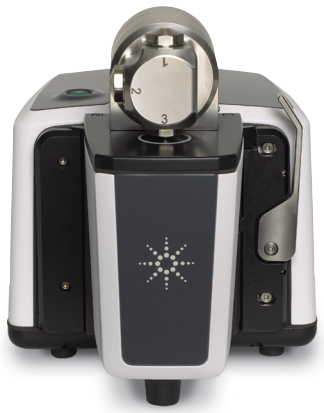

Abstract

A new method has been developed and evaluated for the analysis of oil in water using the Agilent Cary 630 FTIR. This is based on ASTM D7678-11 and the ARPA – APPA Italian guideline 75/2011.

The new method uses Cyclohexane as the extraction solvent, replacing any Carbon Tetrachloride, Freon or fluorinated solvents. It also uses the innovative DialPath liquid sampling system on the Agilent Cary 630 FTIR. These improvements make the analysis safer, faster and less expensive.

Crude oil is a mixture of hydrocarbons with different chemical compositions. It contains hydrocarbons with long and short chains, paraffinic, naphthalenic, aromatics, greases etc. The challenge is to use a suitable liquid- liquid extraction method that uses a more environmentally friendly solvent, to make it possible to quantitate these hydrocarbons rapidly and with less expense.

To use the Agilent Cary 630 FTIR with a 1000 µm DialPath and standard software, and to apply extraction procedure ASTM D7678-11, that uses Cyclohexane as the extraction solvent. Cyclohexane is a cheaper and safer solvent in comparison to more traditional solvents, such as Freon 113 and Carbon Tetrachloride. This allows for a safer, faster and more economical method for the analysis of hydrocarbons.

Introduction

Introduction

Infrared spectroscopy has, for almost 50 years, been one of the fastest and simplest ways to analyse for hydrocarbons in water. This analysis gives results as "total hydrocarbons". When a sample is over the threshold limit, imposed by various protocols (that are different from country to country), it is necessary to reanalyse the sample by gas chromatography, in order to determine the various types of hydrocarbon chain (C_{10} to C_{40}) present.

There are many published procedures that explain different extraction methods and analyses. These include EPA 413.2 (total oil and grease, 1979), EPA 418.1 (total petroleum hydrocarbons, 1994), ASTM D3921 (oil and grease and petroleum hydrocarbons in water, 1996), ASTM D7066-04 (oil and grease, 2004), ISO/TR 11046 (mineral oil content in soil by IR and GC, 1994), ISO 9377-2 (determination of hydrocarbon oil index by GC, 2000) and the new ASTM D7678-11 (total petroleum hydrocarbons in water, 2011). In Italy, the main references are the CNR method 5160 (1976), IRSA method 402.2 (1994) and ARPA – APPA guideline 75/2011.

The innovative technology of Agilent's DialPath Accessory on the Cary 630 (figure 1) facilitates fast FTIR transmission measurements of liquids. It offers several advantages over classic transmission cells. The accessory only requires a very small amount of liquid, with one drop being sufficient for a measurement. It is also very fast and is simple to clean.

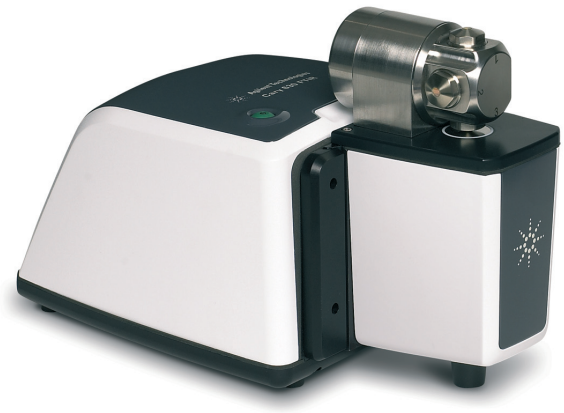

Figure 1: DialPath Accessory

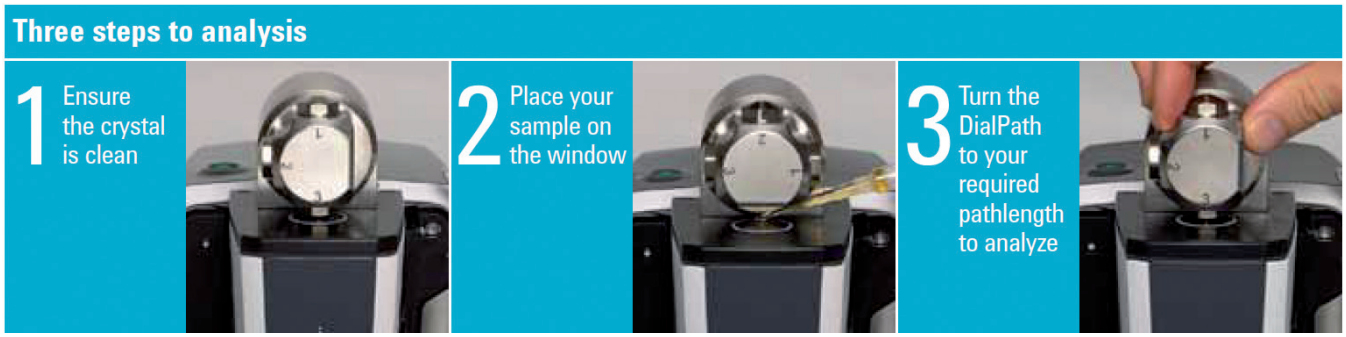

Figure 2: Sample Analysis

Experimental

Sample Preparation

A 500 mL sample of water, acidified with Hydrochloric Acid, is extracted in 3 steps (figure 2) with 15 mL of Cyclohexane (99.9 %, for spectroscopy use). The 3 aliquots of solvent are collected in a 50 mL glass test tube, then reduced in volume using a nitrogen flow evaporator and the final volume adjusted to 0.5 mL with Cyclohexane. Alternatively, the correct volume can be measured by weighing the final volume of solvent and applying a weight correction factor.

The concentrated solvent is then measured on a 1000 µm DialPath, with the background measurement taken on Cyclohexane. The measurement parameters are shown in Table 1.

Parameter	Value
Instrument	Agilent Cary 630
Source	Ceramic
Sampling	1000 µm DialPath™
Optics	ZnSe
Detector	DTGS
Scans	128
Resolution	4 cm^{-1}

Table 1. Measurement Parameters.

Calibration and validation

A set of 14 standards made from a solution of Hexadecane and Isooctane, with the concentrations reported in Table 2, are measured using the same instrumental conditions. The concentrations expressed refer directly to the hydrocarbon (HC) concentrations in 500 mL of water.

Measurement

The spectra for all of the standards are overlaid in Figure 3.
The peak centered at 1380 cm^{-1}, which relates to the methyl group CH bending, directly correlates to the concentration of hydrocarbons. The Cyclohexane solvent has a cyclic structure and does not have any methyl groups, so does not show this peak. The peak area is measured between 1372 and 1386 cm^{-1}, with a baseline between 1352 and 1412 cm^{-1}, as shown in Figure 4.

Name	Total HC ppb
F2std	165.000
Astd	13200.000
Bstd	6600.000
Cstd	3300.000
Dstd	1320.000
Estd	660.000
Fstd	330.000
a std	13200.000
b std	6600.000
c std	3300.000
d std	1320.000
e std	660.000
f std	330.000
f2 std	165.000
zero std	0.000

Table 2. Concentrations of Hydrocarbon (HC) Standards.

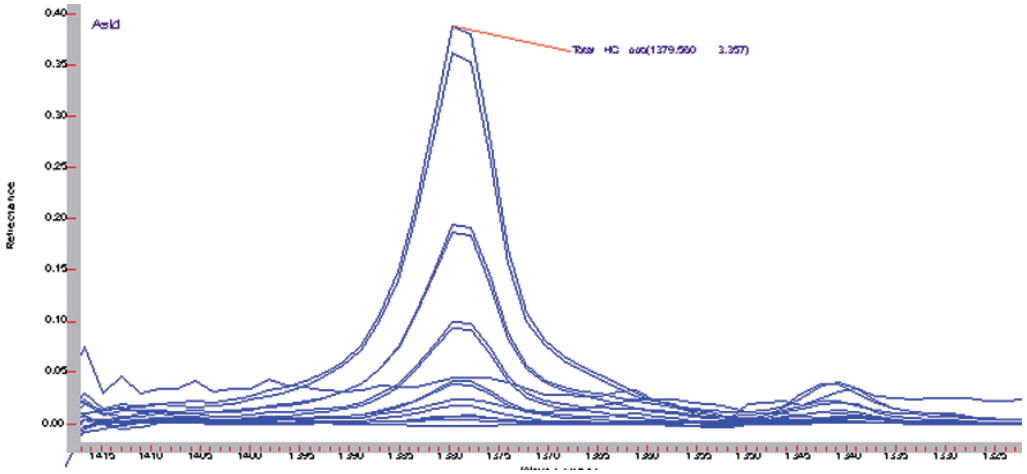

Figure 3: Methyl bending peak on all the standards.

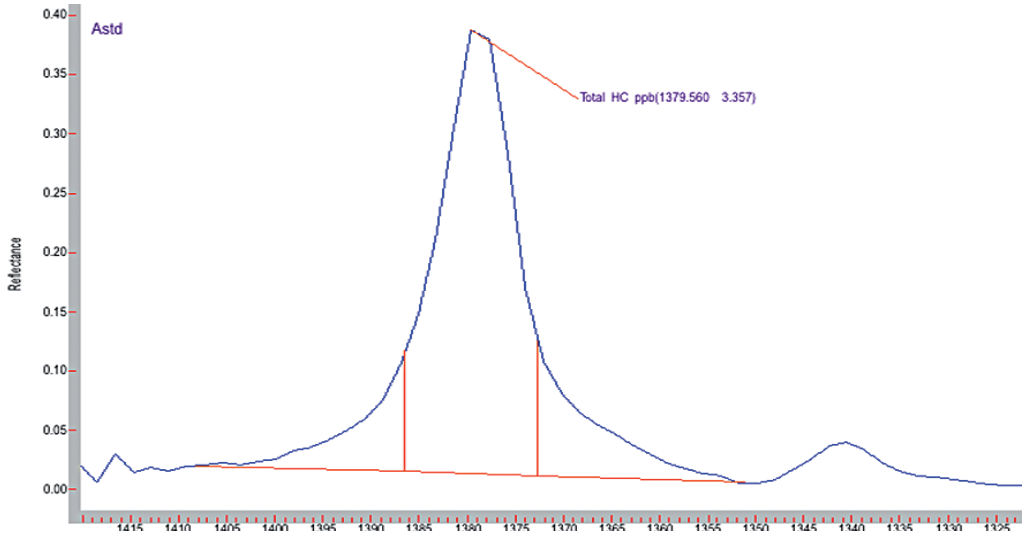

Figure 4: Integration parameters for the methyl group.

The calibration graph is shown in Figure 5.

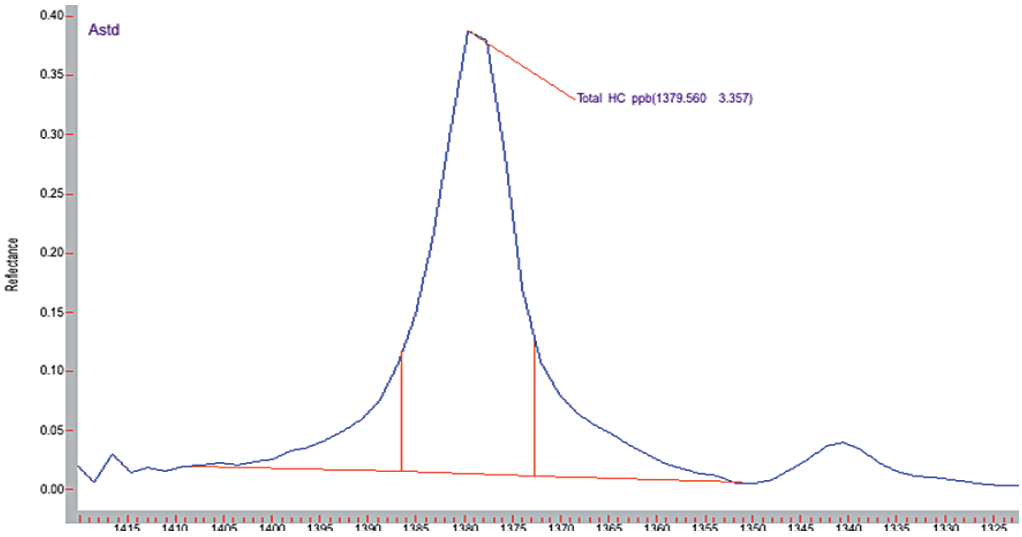

Figure 5: Calibration graph for total HC in water.

Analysis of real samples

Samples are measured as described and read on the calibration curve. The result is the sum of total hydrocarbons and oil and grease, if present. If it is necessary to quantify the amount of hydrocarbons only, the extracted solvent will need to be purified using a Fluorisil column. The purified solvent is then measured and read on the calibration curve. By taking these two measurements, one before and the other after purification, it is also possible to obtain the concentration of oil and grease, if required.

Conclusion

Using method ASTM D7678-11 with this procedure on the Agilent Cary 630 FTIR DialPath allows for the fast determination of total hydrocarbons in water, with similar sensitivity to classic FTIR methods but without the use of fluorinated or chlorinated solvents. Due to the lower density of Cyclohexane in comparison to water, it is possible to perform the extraction directly in the sampling flask, eliminating the need for extraction funnels and improving the recovery of the hydrocarbons.the compounds tested for had RSDs of less than 3 % at this level.

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